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A Fulleropyrrolidine-phthalocyanine dyad for photovoltaic applications

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Abstract

We report on photophysical properties of a novel dyad molecule having as antenna/donor a Zn-phthalocyanine derivative and as acceptor a C₆₀ derivative covalently attached. We found evidences for long living photoinduced electron transfer in solid state. Photovoltaic action of thin film devices of the dyad is demonstrated.

Keywords: solar cells, phthalocyanines, fullerene, photoinduced charge transfer

1. Introduction

Photoinduced electron transfer in organic molecules is an intensively investigated process in natural as well as in artificial systems [1]. Dyads composed of electron acceptor molecules, like fullerenes, covalently linked to photoactive donors are candidates to perform photoinduced electron transfer [2]. The efficient light absorption and charge separation are the fundamental steps for solar energy conversion.

In the present study we have investigated the photophysical properties of a new covalently linked fulleropyrrolidine-phthalocyanine dyad having as antenna/donor a Zn-phthalocyanine derivative and as acceptor a C₆₀ derivative covalently attached [3]. Experimental evidence for photoinduced electron transfer has been observed. Photovoltaic action of thin film devices made from the dyad molecule is reported. The photocurrent spectrum shows photovoltaic activity at 700 nm, the maximum of the terrestrial solar emission spectrum.

2. Experimental

Thin film samples for optical measurements were prepared by spin coating from chlorobenzene solution onto quartz substrates. Photoinduced absorption (PIA) measurements [4] was performed with modulate technique at a frequency of 70 Hz. Photovoltaic devices were built on transparent indium tin oxide (ITO) coated glass, covered with a thin film of PEDOT:PSS. On top of it the active layer (~100–150 nm) was prepared by spin coating from a

toluene solution. The top electrodes were vapor deposited films of LiF and Al.

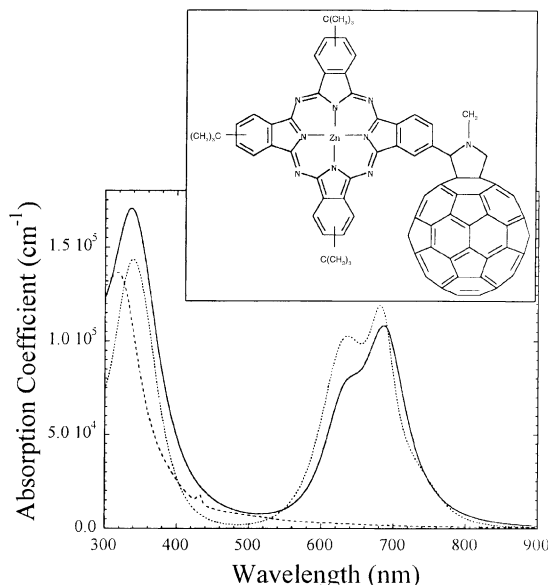


Fig. 1: Absorption coefficient at 300K of thin films of Pc-C60 (continuous line), ZnTBPC (dotted line) and C60-P (dashed line). Inset: Chemical structure of Pc-C60.

3. Results and discussion

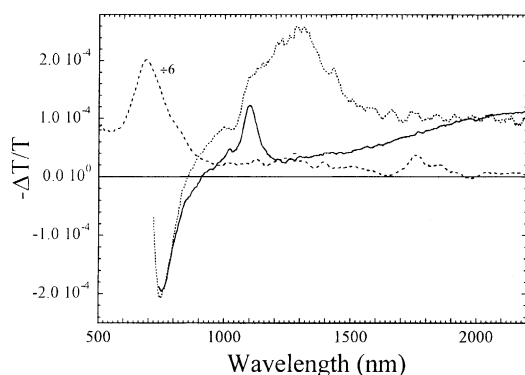
The molecular structure of Pc-C60 is reported in the inset of Fig. 1, the details of the chemical synthesis have been

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reported elsewhere [3]. Similar phthalocyanine-fullerene dyads with larger spacer have been synthesized in the past [5]. However, experimental evidences for charge separation was not found in these compounds.

In Fig. 1 the absorption spectra for the two parent molecules zinc-tetra-tert-butylphthalocyanine (ZnTBPC) and fulleropyrrolidine (C60-P) are reported. The absorption spectrum of Pc-C60 shows noticeable differences from the sum of the spectra of the two parent molecules. The dissimilarities can be ascribed both to a hindered π - π stacking of the phthalocyanines in the Pc-C60 film due the bulky fulleropyrrolidine and/or to ground state charge transfer interaction.

Fig 2: Photoinduced absorption spectra of Pc-C60 dyad, ZnTBPC and C60-P films, continuous, dotted and dashed line, respectively.



Excitations 685 nm and UV multiline Ar⁺ laser. T = 80 K.

Photoinduced absorption spectra of thin films of Pc-C60 dyad and the parent molecules are reported in Fig. 3. The spectrum of ZnTBPC (dotted line) shows a negative signal at 750 nm due to the bleaching of the ground state absorption (see Fig. 2), the large broad absorption feature at ~1300 nm is tentatively assigned to a triplet transition. In Fig. 3 the PIA of a thin film of C60-P dispersed in the inert matrix (dashed line) is also presented. The spectrum is dominated by the triplet transition peaked at 690 nm [6]. The PIA spectrum of Pc-C60 dyad (solid line) has three main features in the spectrum: at 750 nm the bleaching of the ground state absorption, at 1100 nm a narrow absorption peak, and around ~2200 nm a broad absorption feature. The narrow band at 1100 nm is characteristic for the fullerene-derivative anion [6], while the broad feature far in the infrared is of unknown nature. The photoinduced-absorption feature at 1300 nm disappears completely in the dyad spectrum.

The lifetime of the charge separation in Pc-C60 dyad thin films is about 2 ms, which is several order of magnitude longer than has been reported in solution [7]. The long living charge separation opens the possibility to use the dyad as active material in photovoltaic devices.

An important issue for the improvement of the efficiency of photovoltaic devices is the selection and development of new molecules having good overlapping of their absorption spectrum with the terrestrial solar emission spectrum. Since the maximum of the solar photon flux is

around 700 nm, materials like Pc-C60 (Fig. 1), absorbing light in this range are desirable.

Solar cells using thin films of Pc-C60 as active material were fabricated by spin coating from toluene solution in the configuration described in the experimental section. Diode behavior with a rectification ratio of ~10 is observed. Under white light illumination through the ITO electrode with 80 mW/cm² an open circuit voltage of 0.32 V and a short circuit current of 0.2 mA/cm² have been measured. A fill factor of 0.26 and a power conversion efficiency of 0.02% was calculated. The IPCE measurements in Fig. 3 shows that the photocurrent follow the absorption spectra with a maximum in the spectral range around 700 nm.

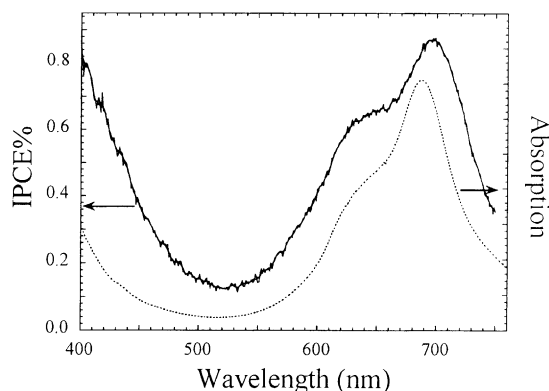


Fig. 3. IPCE measurement of the device using Pc-C60 dyad as active material. The IPCE spectrum is compared with the absorbance spectrum.

4. Conclusions

We report about photophysical characterization and implementation of photoactive devices with a novel dyad molecule having as antenna/donor a Zn-phthalocyanine derivative and as acceptor a C₆₀ derivative. We show evidence for long living photoinduced charge separation, which is a prerequisite for the application in photovoltaic devices. Due to the absorption maximum of the dyad at 700 nm, this dyad appear to be promising for solar applications.

5. Acknowledgements

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